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(54) Abstract Title

Anti-tarnishing of copper or copper alloy

(57) An anti-tarnishing solution for copper or copper alloy material which can produce a treated surface having outstanding heat resistance as well as anti-tarnishing effect in ordinary environment, with excellent adhesion to resin at low temperatures comprises a silane coupling agent and a metal nobler than copper or a salt of the metal as major constituents and water or an organic solvent, and further optionally comprising a pH buffering agent and/or surfactant. The anti-tarnishing treatment is carried out by dipping the copper or copper alloy in the anti-tarnishing solution or by sprinkling or spraying the solution over the object. The metal may be Ag, Au, Pt, Pd, Rh, Ru, or Os and the salt may be salt of these metals. Numerous different silanes may be used.

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**Anti-tarnishing solution and a method for preventing tarnishing
of copper or copper alloy**

This invention relates to an anti-tarnishing solution and a method for preventing tarnishing of copper or copper alloy. This invention is particularly, but not exclusively, suitable to be used for lead frames, TABs, printed circuit boards, etc.

Blanks usually of copper or copper alloy for electronic components such as lead frames and TABs are often subjected to high speed partial silver plating. Any unwanted silver deposit is selectively dissolved away using a desilvering (silver stripping) solution for removal. The blanks then are moulded and sealed in resin. Thus the process involves dipping in acid or alkali solution, temporary storage, heating, bonding, resin moulding and sealing, etc. The blanks for lead frames, TABs, etc., therefore, are required to have properties such as bondability and resistance to heat and chemical attacks.

Moreover, they must not tarnish while being transported or stored or upon heating.

For lead frames various methods for preventing their tarnishing have hitherto been proposed. For example, Japanese Patent Application Kokai No. 4-160173 discloses a copper-tarnishing preventing agent comprising 5-methyl-1H-benzotriazole, etc. Patent Application Kokai No. 6-350000 introduces an agent comprising an alkoxysilane coupling agent and an organic solvent for the surface treatment of lead frames. The former agent exhibits outstanding tarnishing-preventing effects at normal temperatures but lacks heat resistance so that the oxide film it forms readily comes off on heating and reduces the adhesion to resin. The latter, by contrast, enhances the adhesion to resin and yet it shows no anti-tarnishing effect at normal temperatures and inadequate heat resistance, either.

In view of these, the present inventors previously proposed in Patent

Application No. 8-122343 "an anti-tarnishing solution prepared by adding a metal nobler than copper or a salt of the metal to a solution of a heterocyclic compound which contains nitrogen or sulfur or both in the molecule and which acts as a copper inhibitor." That anti-tarnishing solution which is one of a type that depends on replacement with a noble metal, produces a replacement layer that excels in heat resistance as well as in anti-tarnishing effect in an ordinary environment. However, its low adhesion to resin at low temperatures has been pointed out. To increase the adhesion, it requires heat treatment prior to bonding.

In order to provide improvements to the prior art the present inventors have made intensive and extensive research. As a result, it has now been found that the both requirements for anti-tarnishing effect and low-temperature adhesion to resin can be met by dipping a copper or copper alloy stock in a solution containing a silane coupling agent and a metal nobler than copper or a salt of the metal as its major constituents.

According to one aspect of this invention there is provided an anti-tarnishing solution for copper or copper alloy characterised by including a silane coupling agent and a metal nobler than copper or a salt of the metal as major constituents and water or an organic solvent as a solvent.

The phrase "a metal nobler than copper" as used herein means a metal whose ionisation tendency is less than that of copper.

Preferably the metal nobler than copper or the salt of the metal is one or more metals selected from the group consisting of silver, gold, platinum, palladium, rhodium, ruthenium, and osmium or a salt or salts of such metals.

The silane coupling agent may be one or more compounds selected from the group consisting of aminosilane compounds, epoxysilane compounds, vinylsilane compounds, mercaptosilane compounds, alkylsilane compounds, halogenosilane compounds, polymer type silane compounds, and azolesilane

compounds or a derivative or derivatives of such compounds.

The solution may contain per litre, from 0.1mg to 100g of the silane coupling agent and from 10mg to 100g of the metal nobler than copper or the salt of the metal.

The solution may further comprise a pH buffering agent, a surfactant, or both.

According to another aspect of this invention there is provided a method for preventing tarnishing of copper or copper alloy characterised by either dipping the copper or copper alloy into, or sprinkling or spraying the same with, an anti-tarnishing solution for copper or copper alloy characterised by comprising a silane coupling agent and a metal nobler than copper or a salt of the metal as major constituents and water or an organic solvent as a solvent.

Preferably the metal nobler than copper or the salt of the metal is one or more metals selected from the group consisting of silver, gold, platinum, palladium, rhodium, ruthenium, and osmium or a salt or salts of such metals.

The silane coupling agent may be one or more compounds selected from the group consisting of aminosilane compounds, epoxysilane compounds, vinylsilane compounds, mercaptosilane compounds, alkylsilane compounds, halogenosilane compounds, polymer type silane compounds, and azolesilane compounds or a derivative or derivatives of such compounds.

The solution may contain per litre, from 0.1mg to 100g of the silane coupling agent and from 10mg to 100g of the metal nobler than copper or the salt of the metal.

The anti-tarnishing solution may further comprise a pH buffering agent, a surfactant, or both.

The surface of the copper or copper alloy may be roughened or oxidized prior to the anti-tarnishing treatment.

The copper or copper alloy may be roughened by a plating, chemical polishing, electropolishing, abrasive-paper polishing, abrasive blasting, or honing technique.

The copper or copper alloy may be oxidised by dipping in an oxidizer solution, by electrolytic oxidation, or by heating.

One embodiment of this invention has an advantage that it provides an anti-tarnishing solution and a method for preventing tarnishing copper or copper alloy, whereby excellent anti-tarnishing effects and heat resistance are achieved in ordinary environment and great adhesion to resin is attained at low temperatures.

The anti-tarnishing solution according to this invention comprises "a silane coupling agent and a metal nobler than copper or a salt of the metal" as its major constituents.

The silane coupling agent may be any such agent which comprises one or more compounds selected from the group consisting of aminosilane compounds, epoxysilane compounds, vinylsilane compounds, mercaptosilane compounds, alkylsilane compounds, halogenosilane compounds, polymer type silane compounds, and azolesilane compounds or a derivative or derivatives of such compounds. Examples are aminosilane, epoxysilane, imidazolesilane, benzimidazolesilane, and benzotriazolesilane.

The anti-tarnishing solution of this invention contains one or more silane coupling agents selected from the above group, desirably at the rate of from 0.1mg to 100g per litre (more desirably from 10mg to 10g per litre). The range is so specified, since if the proportion of the silane coupling agent is less than 0.1mg per litre the anti-tarnishing effect is insufficient, and if the

proportion is more than 100g per litre no more favourable effect can be expected.

In the anti-tarnishing solution of this invention, the metals nobler than copper and the salts of such metals can achieve approximately equal actions and effects. Desirably, one or more metals selected from the group consisting of silver, gold, platinum, palladium, rhodium, ruthenium, iridium, and osmium or a salt or salts of such metals are used. The most commonly used are silver salts, such as silver cyanide, silver potassium cyanide, silver sodium cyanide, and silver nitrate; gold potassium cyanide; diammine-dichloro-palladium; rhodium sulfate; etc.

One or more metals nobler than copper or one or more salts chosen are contained in the solution desirably at the ratio of from 10mg to 100g per litre (more desirably at the rate of from 100mg to 10g per litre). The range is so specified because a proportion of a metal or its salt of less than 10mg per litre produces too small a metal deposit to achieve an appreciable improvement in heat resistance, while a proportion of more than 100g per litre does not promise an accordingly enhanced effect.

Water is usually used as a solvent for the major constituents, silane coupling agent and metal or metals nobler than copper or their salts. When the major constituents are difficult to dissolve in water, an organic solvent such as alcohol or ketone is added according to the necessity.

Also, when necessary, the anti-tarnishing solution of this invention may contain a buffering agent or surfactant or both.

As a buffering agent, a boric acid, phosphoric acid, or organic acid type may be employed. Such an agent is added at the rate of from 0.1 to 100g per litre, preferably from 1 to 50g per litre.

As a surfactant, any of anionic, cationic, non-ionic surfactant or their

mixture may be used. The amount to be added ranges from 1 μ g to 10g per litre, preferably from 10 μ g to 1g per litre.

The pH of the anti-tarnishing solution according to this invention is not specially limited if only it permits dissolution of the above-mentioned constituents.

The temperature of the anti-tarnishing solution is desirably in the range from 5 to 80°C, more desirably from 10 to 40°C.

The treatment of copper or copper alloy with the anti-tarnishing solution of this invention is performed by dipping the copper or copper alloy as a base into a bath of the solution or by sprinkling or spraying the solution over the copper or alloy.

The duration of the treatment is between 0.1 second to 10 minutes, preferably between 1 and 60 seconds.

The treatment produces an excellent anti-tarnishing effect, even on the surface from which an electrodeposited silver layer has been selectively removed using a desilvering solution.

The anti-tarnishing treatment may be preceded by roughening or oxidation of the copper or its alloy surface to enhance its adhesion to resin.

Roughening of the material may be carried out by chemical polishing, electropolishing, abrasive-paper polishing, abrasive blasting, honing, or plating. To be more concrete, any of the following procedures may be adopted for the roughening purpose:

a) Chemical polishing

Dipping in a solution of 100g ammonium persulfate per litre for 30

seconds.

b) Electropolishing

Electrolysis in a 70% phosphoric acid solution, making copper the anode, at 2V for 10 minutes.

c) Abrasive-paper polishing

Polishing with #600 SiC abrasive paper.

d) Abrasive blasting

Blasting with #100 alumina particles at a pressure of 3 kg/cm².

e) Honing

Honing with #100 alumina particles at a pressure of 3 kg/cm².

f) Plating

Electroplating in a bath containing 30g copper cyanide, 45g potassium cyanide, and 4g potassium hydroxide per, all per litre, at a cathode current density of 10A/dm² for 30 seconds.

Oxidation of the material may be effected by dipping in an oxidizer solution, electrolysis heating. Exemplary oxidation procedures are as follows:

a) Dipping in oxidizer solution

Dipping in an oxidizer solution which contains 30g sodium hypochlorite, 15g phosphoric acid, and 10g sodium hydroxide, all per litre, for 30 seconds.

b) Electrolysis

Anodic electrolysis in a solution containing 100g sodium hydroxide per litre, at an anode current density of 5 A/dm² for 30 seconds.

c) Heating

Heat treatment at 250°C for one minute.

The roughening or oxidation conducted prior to the anti-tarnishing treatment further enhances the adhesion of the copper or copper alloy material to resin in the subsequent step of resin molding.

The base material to be treated for the prevention of tarnishing in accordance with this invention is a copper or copper alloy material such as copper foil for lead frames, TABs, or printed circuit boards. The term "copper or copper alloy" as used herein means, of course, not only material wholly of copper or copper alloy alone but also all materials surfaced with copper or copper alloy, including iron or iron alloy, nickel or nickel alloy, or other metal less noble than silver coated with copper by strike plating.

In accordance with this invention, copper or a copper alloy is contacted with an "anti-tarnishing solution for copper or copper alloy characterised by comprising a silane coupling agent and a metal nobler than copper or a salt of the metal as major constituents and water or an organic solvent as a solvent" by dipping, sprinkling, spraying or the like. In this way, an anti-tarnishing function and adhesion-enhancing function are imparted to the copper or copper alloy surface, for the reasons now to be explained.

The contact of a copper or copper alloy material with an anti-tarnishing solution according to this invention does not form an oxide film on the copper or copper alloy surface but does form a thin uniform layer, from about 10 to 1000Å thick, of a replacement film of a "metal nobler than copper" on the

surface. The replacement film of the "metal nobler than copper" thus formed protects the copper or copper alloy from its transportation and storage environments, preventing its tarnishing. Moreover, the replacement film of a "metal nobler than copper" is sufficiently heat-resistant to prevent both the "oxidation of itself" and "oxidation of the copper or copper alloy surface" even in environments where temperature is relatively high. There is no possibility of any oxide film coming off.

Needless to say, the formation of the replacement film of a "metal nobler than copper" does not deprive the copper or copper alloy material of its inherent desirable properties.

The silane coupling agent, one of the major constituents of the anti-tarnishing solution according to the invention, causes uniform replacement of copper with a "metal nobler than copper" and, owing to its coupling effect, ensures strong bond between the metal and resin.

Consequently, protection of copper or copper alloy against tarnishing, increased adhesion to resin, and improvements in resistance to heat and moisture are all achieved together.

The roughening of the material surface prior to the anti-tarnishing treatment produces an anchoring effect, which enhances the adhesion. The oxidation prior to the anti-tarnishing treatment again improves the adhesion between the metal and epoxy resin because it increases the number of hydrogen bonds between the resin and the surface oxide or hydroxide on the metal surface that are responsible for the adhesion.

This invention is illustrated by its examples as compared with comparative examples as follows:

Lead frame blanks of a copper-strike-plated copper alloy (99.7% Cu-2.0% Sn-0.2% Ni-0.03%P) were washed with pure water and were dipped in a

pretreating solution which contained 100mg 2-thiobarbituric acid as a replacement inhibitor per litre and which had been adjusted to pH 10, at a bath temperature of 30°C for 10 seconds. The blanks were then washed with pure running water for 20 seconds and were silver plated by dipping, at $Dk=70A/dm^2$ for 10 seconds, in a high speed silver electroplating solution which contained

$KAg(CN)_2$: 130 g/l

K_2HPO_4 : 100 g/l

and had been adjusted to pH 8.5.

The silver-plated lead frame blanks were then washed with pure water, and their silver-plating layer except for the middle part was dissolved away using a commercially available desilvering agent. The blanks were again washed with pure water and were dipped in varied anti-tarnishing solutions shown in Table 1.

Prior to the dipping in the anti-tarnishing solutions, some specimens were roughened on surface by chemical polishing plating, or abrasive blasting.

The chemical polishing was performed by dipping in a solution containing 100 g ammonium persulfate per litre for 30 seconds.

For the plating, electroplating was carried out using a bath which contained 30g copper cyanide, 45g potassium cyanide, and 4g potassium hydroxide per litre at a cathode current density of $10 A/dm^2$ to obtain two different plate thicknesses of $0.2\mu m$ and $3.0\mu m$.

The abrasive blasting was done using #100 alumina particles at a pressure of $3kg/cm^2$.

The specimens dipped in the anti-tarnishing solutions of Table 1 were

immersed in boiling pure water for 10 minutes, and their strike-plated surfaces were visually inspected for any indication of tarnishing.

The heat treatment whereby the specimens were "immersed in boiling pure water for 10 minutes" is a commonly employed treatment as an acceleration measure for a test of standing in the air.

Also, the anti-tarnishing treated specimens were evaluated for their heat resistance by measuring the "temperature at which a copper oxide film in a tape test is peeled off by a 30-minute heat treatment."

The specimens were further tested for the evaluation of their adhesion to resin at low and high temperatures. For the low-temperature adhesion to resin, each specimen was not heated before being bonded to the moulding resin. For the high-temperature adhesion, each specimen was heated at 250°C for 5 minutes beforehand.

In each case, "the bond strength that the specimen shared with an epoxy moulding resin" was measured. The moulding resin was cured at 175°C for 5 hours.

As comparative examples, similar tests were conducted with the exception that an anti-tarnishing solution which contained imidazole in place of a silane coupling agent as a major constituent was used (Comparative Example 1) or that an anti-tarnishing solution was used which contained epoxysilane as a silane coupling agent but used no salt of metal nobler than copper (Comparative Example 2). The results were evaluated. These results are also given in Table 1.

It was confirmed from the results summarised in Table 1 that the treatments with the anti-tarnishing solutions according to this invention produced very good anti-tarnishing effects and the treated surfaces showed great heat resistance, from 380 to 400°C in terms of the temperature for tape

peeling from the oxide film on the surfaces. Every test specimen exhibited great adhesion to resin of more than 40kg/cm^2 at elevated temperature. In addition, each showed satisfactorily great low-temperature adhesion above 25kg/cm^2 .

When the anti-tarnishing solution used contained imidazole in place of a silane coupling agent as a major constituent (Comparative Example 1), the specimen showed adequate high-temperature adhesion to resin but its low-temperature adhesion was only 15.4kg/cm^2 . When the anti-tarnishing solution that contained epoxysilane as a silane coupling agent but did not contain a salt of metal nobler than Copper was used (Comparative Example 2), the heat resistance was low at 320°C and the high-temperature resin adhesion of 22.5kg/cm^2 was unsatisfactory either.

As described above, this invention provides an anti-tarnishing solution for copper or copper alloy material which can produce a treated surface having outstanding heat resistance as well as anti-tarnishing effect in ordinary environment, with excellent adhesion to resin at both high and low temperatures. Thus this invention brings about industrially valuable effects by contributing greatly to the reliability of copper or copper alloy materials for electronic components, such as lead frames, TABs, and printed circuit boards.

[Table 1]

		The present invention							Comparative Example	
		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comp. Ex. 1	Comp. Ex. 2
Pre-treatment		None	Chemical polishing	None	Plating 0.2 μ m	Plating 1.0 μ m	Abrasive blasting	None	None	None
Anti-tarnishing solution	Main constituent	Amino-silane, 1 g/l	Epoxy-silane, 1 g/l	Imido-azole-silane, 1 g/l	Imido-azole-silane, 1 g/l	Imido-azole-silane, 1 g/l	Imido-azole-silane, 1 g/l	Imido-azole-silane, 1 g/l	Imido-azole-silane, 1 g/l	Epoxy-silane, 1 g/l
	Salt of metal nobler than copper	Silver potassium cyanide, 2 g/l	Silver potassium cyanide, 2 g/l	Silver potassium cyanide, 2 g/l	Silver potassium cyanide, 2 g/l	Silver potassium cyanide, 2 g/l	Gold potassium cyanide, 2 g/l	Diamminedichloropalladium, 2 g/l	Silver potassium cyanide, 2 g/l	None
	Solvent	Methanol, 10 ml/l	Methanol, 10 ml/l	Methanol, 10 ml/l	Methanol, 10 ml/l	Methanol, 10 ml/l	Methanol, 10 ml/l	Methanol, 10 ml/l	None	Methanol, 10 ml/l
	Buffering agent	Potassium tetraborate, 5 g/l	Potassium tetraborate, 5 g/l	Potassium tetraborate, 5 g/l	Potassium tetraborate, 5 g/l	Potassium tetraborate, 5 g/l	Potassium tetraborate, 5 g/l	Potassium tetraborate, 5 g/l	Potassium tetraborate, 5 g/l	Potassium tetraborate, 5 g/l
	Surfactant	Polyoxyethylene nonyl phenyl ether, 1 mg/l	None	None	Polyoxyethylene nonyl phenyl ether, 1 mg/l	None	None	None	None	None
Anti-tarnishing treatment conditions	pH	12.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	Bath temp, °C	25	25	25	25	25	25	25	25	25
	Time, sec	10	10	10	10	10	10	10	10	10
	Method	Dip	Dip	Dip	Dip	Dip	Dip	Dip	Dip	Dip

(Continued)

		The present invention							Comparative	
		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comp. Ex. 1	Comp. Ex. 2
Results of evaluation	Anti-tarnishing	Good	Good	Good	Good	Good	Good	Good	Good	Good
	Heat resistance	380°C	400°C	400°C	400°C	440°C	400°C	400°C	380°C	320°C
	Low-temp resin adhesion, kg/cm ²	27.9	27.3	29.8	35.6	38.2	30.1	28.8	15.4	30.4
	High-temp resin adhesion, kg/cm ²	40.3	40.6	42.1	40.7	50.3	45.2	43.5	40.2	22.5

CLAIMS

1. An anti-tarnishing solution for copper or copper alloy comprising a silane coupling agent and a metal nobler than copper or a salt of the metal as major constituents and water or an organic solvent as a solvent.
2. A solution according to claim 1 wherein the metal nobler than copper or the salt of the metal is one or more metals selected from the group consisting of silver, gold, platinum, palladium, rhodium, ruthenium, and osmium or a salt or salts of such metals.
3. A solution according to claim 1 or 2 wherein the silane coupling agent is one or more compounds selected from the group consisting of aminosilane compounds, epoxysilane compounds, vinylsilane compounds, mercaptosilane compounds, alkylsilane compounds, halogenosilane compounds, polymer type silane compounds, and azolesilane compounds or a derivative or derivatives of such compounds.
4. A solution according to claim 1, 2, or 3 which contains, per litre, from 0.1 mg to 100 g of the silane coupling agent and from 10 mg to 100 g of the metal nobler than copper or the salt of the metal.
5. A solution according to any of claims 1 to 4 further comprising a pH buffering agent, a surfactant, or both.
6. A method for preventing tarnishing of copper or copper alloy comprising either dipping the copper or copper alloy into, or sprinkling or spraying the same with, an anti-tarnishing solution for copper or copper alloy which comprises a silane coupling agent and a metal nobler than copper or a salt of the metal as major constituents and water or an organic solvent as a solvent.
7. A method according to claim 6 wherein the metal nobler than copper or the salt of the metal is one or more metals selected from the group consisting

of silver, gold, platinum, palladium, rhodium, ruthenium, and osmium or a salt or salts of such metals.

8. A method according to claim 6 or 7 wherein the silane coupling agent is one or more compounds selected from the group consisting of aminosilane compounds, epoxysilane compounds, vinylsilane compounds, mercaptosilane compounds, alkylsilane compounds, halogenosilane compounds, polymer type silane compounds, and azolesilane compounds or a derivative or derivatives of such compounds.

9. A solution according to claim 6, 7, or 8 which contains, per litre, from 0.1 mg to 100 g of the silane coupling agent and from 10 mg to 100 g of the metal nobler than copper or the salt of the metal.

10. A method according to any of claims 6 to 9 wherein the anti-tarnishing solution further comprises a pH buffering agent, a surfactant, or both.

11. A method according to any of claims 6 to 10 wherein the surface of the copper or copper alloy is roughened or oxidized prior to the anti-tarnishing treatment.

12. A method according to claim 11 wherein the copper or copper alloy is roughened by a plating, chemical polishing, electropolishing, abrasive-paper polishing, abrasive blasting, or honing technique.

13. A method according to claim 11 wherein the copper or copper alloy is oxidized by dipping in an oxidizer solution, by electrolytic oxidation, or by heating.

14. An anti-tarnishing solution for copper or copper alloy substantially as herein described.

15. A method for preventing tarnishing of copper or copper alloy

substantially as herein described.

16. Any novel subject matter or combination including novel subject matter disclosed herein, whether or not within the scope of or relating to the same invention as any of the preceding claims.



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Claims searched: 1-14

Examiner: Peter Beddoe
Date of search: 29 April 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C7U; C7F (FHAA, FHAB)

Int Cl (Ed.6): C23C (18/42, 18/44, 22/00, 22/05, 22/48, 22/52, 22/68); C23F 11/10

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X,Y	WO 96/36747 A1 (HENKEL) see esp exs	X=1 at least Y=1-4,6,7 at least
Y	WO 96/17975 A1 (ALPHA) see esp p15 lines 19-26. Exs & claim 17	Y=1-4,6,7 at least
Y	WO 96/11751 A1 (RD CHEMICALS) see esp exs	Y=1-4,6,7 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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